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Novel Synthesis of Sulfonated Silicones

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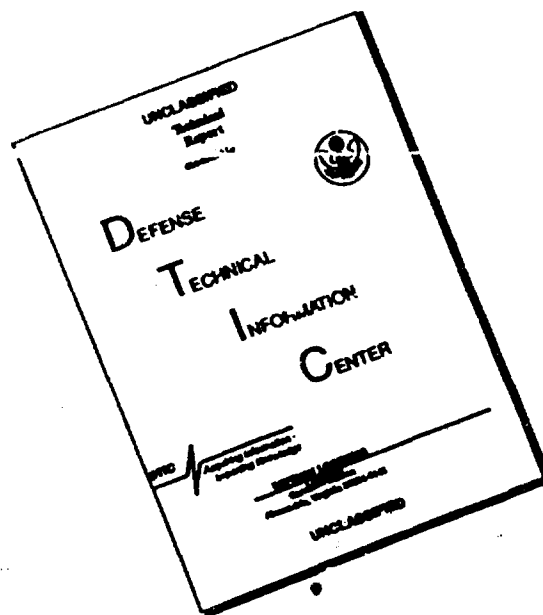
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# Novel Synthesis of Sulfonated Silicones

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## Abstract

Treatment of silyl ketene acetal-derivatized silicones with trimethylsilyl sulfonyl chloride, followed by hydrolysis in mild base, affords sulfonated silicones in high yield. Silicones having about 90% sulfonate pendants are water soluble, and may be used as new dopants for conducting polymers. These polyanions may also have use as polymer electrolytes having exclusively cation conduction.

(keywords: synthesis, modification, sulfonation, water soluble, polysiloxanes, silicones, polyelectrolytes, trimethyl silyl sulfonyl chloride)

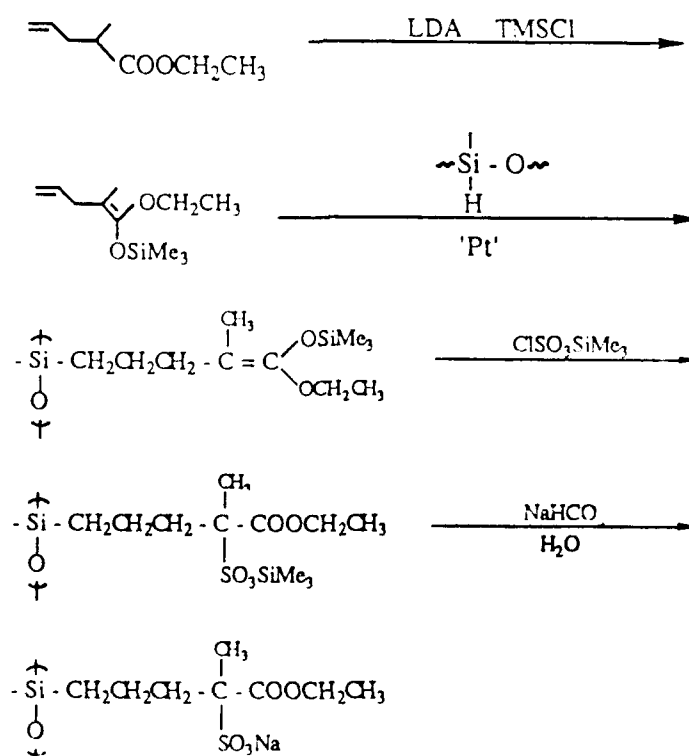


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## Introduction.

Polysiloxanes are known for their useful properties which include flexibility,<sup>[1]</sup> heat and oxygen resistance,<sup>[2]</sup> biocompatibility<sup>[3]</sup> and gas permeability<sup>[4]</sup>. There is considerable interest in their use as polymer electrolytes as the flexible backbone can facilitate ion transport. We have been interested in preparing sulfonated silicones which may function as cation transporters. In addition, we are interested in water-soluble silicones for biomedical applications.

In 1989, Smid et al.<sup>[5]</sup> developed the method to prepare siloxane polymers with pendant sulfonated groups via sulfonation of epoxide-functionalized siloxanes. This approach has as limitations long reaction times and the use of aqueous-based sulfonating agents (sodium bisulfite in this case). We wish to report a simple method of sulfonation which takes place in organic solutions, and is thus facile with initially water-insoluble siloxanes. Advantage is taken of the reaction of silyl ketene acetal-modified siloxanes, developed in our laboratory,<sup>(6)</sup> with trimethyl silyl sulfonyl chloride.<sup>(7)</sup> The trimethyl silyl sulfonate is then converted to the corresponding ionic



Scheme 1

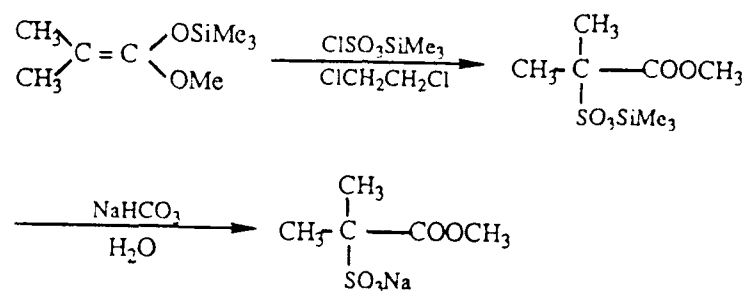
sulfonate by hydrolysis in mild base such as sodium bicarbonate. The chemistry is summarized in Scheme 1. The resulting polymers are water-soluble. We describe here the details of the synthesis and preliminary characterization of the polymers.

### **Experimental.**

A. Materials: Poly(methyl hydrosiloxane), PMHS, was acquired from Petrarch and had a number average molecular weight of approximately 4500 - 5000 g/mol according to the supplier. Platinum divinyl tetramethyl disiloxane complex was acquired from Petrarch and stored in refrigerator. Trimethyl silyl chloride TMSCl, ethyl 2-methyl 4-pentenoate and methyl trimethyl silyl dimethyl ketene acetal MTDA were acquired from Aldrich and distilled prior to use. Trimethyl silyl sulfonyl chloride, lithium diisopropyl amide, sodium bicarbonate, anhydrous dichloroethane and anhydrous ether were acquired from Aldrich and used as received. Toluene and THF were distilled from sodium benzophenone. Spectra/Por dialysis membrane was acquired from Polysciences and had a molecular weight cut off of approximately 3500.

B. Measurements: Elemental analyses were performed by Schwarzkopf Laboratory, Woodside, N.Y..  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra were obtained on a Varian XL-200 spectrometer. Solvent peaks were used as the internal standard. FT-IR spectra were recorded on a Perkin Elmer 1850 FT-IR. Melting points were determined on a Mel-Temp melting point apparatus and were uncorrected.

C. Model reaction: The reaction of MTDA with trimethyl silyl sulfonyl chloride (Scheme 2) was chosen as a model reaction.



Scheme 2

a. Reaction of MTDA with trimethyl silyl sulfonyl chloride.

To a solution of MTDA(2.92g, 20mmol) in 100ml anhydrous dichloroethane in dry box, trimethyl silyl sulfonyl chloride(3.77g, 20mmol) was added dropwise. The reaction mixture was standed for 2hr in dry box. Dichloroethane and byproducts were removed using a rotary evaporator through a drying tube and then kept at 70°C, 4mmHg for another 2hr. The yield of methyl (2-methyl-2-trimethyl silyl sulfonyl) propanoate was 89%. This material is referred to as TMSSP.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (in ppm from  $\text{CHCl}_3$ ), 3.39 (s, 1 $\text{CH}_3$ ), 1.51 (s, 2 $\text{CH}_3$ ), 0.19 (s, 3 $\text{CH}_3$ ).

b. hydrolysis of TMSSP

To a saturated sodium bicarbonate aqueous solution, TMSSP was added dropwise with continuous stirring until the pH dropped to 7. Water was removed by rotary evaporator and then the sample was kept in high vacuum at 60°C overnight. Methyl (2-methyl-2-sodium sulfonyl) propanoate was obtained as a white solid. The conversion of the reaction is 99%. the compound is referred to as SSP.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  ( in ppm from DHO), 3.60 (s, 1 $\text{CH}_3$ ), 1.39 (s, 2 $\text{CH}_3$ ).

$^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  (in ppm from DSS) 176.0, 67.1, 23.7.

**D. Synthesis of ethyl trimethylsilyl-2-methyl-2-alkyl ketene acetal(ETMA)** A 500ml three-necked round bottomed flask was fitted with a reflux condenser, magnetic stirring bar, rubber septum, and a gas inlet. The apparatus was connected through the gas inlet to an argon source and reflux

condenser to a bubbler. After the flask was flame-dried and flushed with argon, it was charged with 250ml of THF and lithium diisopropylamide(200mmol). The flask was immersed in an ice-salt bath and cooled to  $-10^{\circ}\text{C}$ , and over a period of about 5min, 2-methyl-4-pentenoate(32.6ml, 200mmol) was added dropwise through an additional funnel over a 10min period. The solution was stirred for an additional 30 min at  $0^{\circ}\text{C}$ . At this point, distilled trimethylsilylchloride(40ml, 315mmol) was rapidly introduced with a syringe through the septum. After the addition was complete(Ca 30s) the solution was stirred for an additional 1h at room temperature. Solvent was removed using a rotary evaporator and the residue was treated with 200ml of pentane. The slurry was filtered and the filtrate was concentrated on a rotary evaporator and then distilled at reduce pressure. The product, ethyl trimethylsilyl 2-methyl-2-alkyl ketene acetal, was distilled at  $79^{\circ}\text{C}$ (15mmHg). The yield was 92%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (in ppm from  $\text{CHCl}_3$ ), 5.70 (m, 1H, allyl), 4.92 (m, 2H, allyl), 3.75 (m, 2H,  $\text{OCH}_2\text{CH}_3$ ), 2.65 (q, 2H,  $-\text{CH}_2-$ ), 1.51 (d, 3H,  $\text{CH}_3$ ), 1.18 (m, 3H,  $\text{OCH}_2\text{CH}_3$ ), 0.16(d, 9H,  $\text{SiMe}_3$ ).

E. Hydrosilation of poly(methylhydrosiloxane) with ETMA To a mixture of PMHS(6g, 100mmol) and ETMA(21.4g, 100mmol) in 100ml dry toluene, several drops of platinum divinyl tetramethyl disiloxane solution(3% in xylene) was added. The mixture was refluxed under argon at  $60^{\circ}\text{C}$  for 24hr. The extent of reaction was followed by IR spectroscopy. The remaining Si-H groups were reacted in a similar fashion for additional 6hr by adding a slight excess of 1-hexene. Solvent and unreacted ETMA were removed at reduce pressure with rotary evaporator first, and the resulting liquid was kept under high vacuum for 24hr. The product, poly[(5-ethoxy-5-trimethylsilyl-4-methylpentyl-4-ene) methylsiloxane] referred to PSSKA, was a colorless, viscous liquid.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  (in ppm from  $\text{C}_6\text{D}_5\text{H}$ ), 3.82 (m, 2H,  $\text{OCH}_2\text{CH}_3$ ), 2.38 (m, 2H,  $\text{CH}_2-\text{C}=\text{C}-$ ), 1.88 (d, 3H,  $\text{CH}_3$ ), 1.80 (m, 2H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2$ ), 1.22 (m, 3H,

$\text{OCH}_2\text{CH}_3$ ), 0.83 (m, 2H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2$ ), 0.45 (s, 3H,  $\text{Si}(\text{CH}_3)\text{O}$ ), 0.17(d, 9H,  $\text{SiMe}_3$ ).

$^{13}\text{C}$  NMR  $\delta$  (in ppm from  $\text{C}_6\text{D}_6$ ), 149.8, 96.0, 62.4, 34.9, 22.6, 18.3, 15.5 14.6, 0.7, 0.2.

F. Reaction of ketene acetal-modified polysiloxane with trimethylsilyl sulfonyl chloride A 100ml one-necked round bottomed flask was baked by flame and flushed with dry argon, then equipped with magnetic stirring bar in a dry box. The flask was charged with 50ml anhydrous dichloroethane and PSSKA(5.48g, 20mmol). After that, trimethyl silyl sulfonyl chloride(5.0g, 26.5mmol) was added dropwise, with continuous stirring, over a 30 min period. The solution was stirred for an additional 4hr. Solvent and unreacted trimethyl silyl sulfonyl chloride was removed by distillation at reduced pressure. The resulting polymer, abbreviated as  $\text{PSSO}_3\text{TMS}$ , was a lightly brown color, viscous liquid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (in ppm from  $\text{CHCl}_3$ ), 4.22 (q, 2H,  $\text{COOCH}_2\text{CH}_3$ ), 2.35 (m, 2H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2$ ), 1.68 (s, 3H,  $\text{CH}_3$ ), 1.26 (t, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.09 (m, 2H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2$ ), 0.82 (m, 2H,  $\text{SiCH}_2\text{CH}_2\text{CH}_2$ ), 0.63 (s, 3H,  $\text{SiCH}_3$ ), 0.37(s, 9H,  $\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ (in ppm from  $\text{CDCl}_3$ ), 169.8, 74.9, 65.1, 40.7, 39.2, 20.5, 19.6, 16.4, 2.5, 0.6.

G. Hydrolysis of  $\text{PSSO}_3\text{TMS}$  To a 200ml saturated sodium bicarbonate aqueous solution,  $\text{PSSO}_3\text{TMS}$  was added dropwise with continuous stirring. After addition, the solution was concentrated on a rotary evaporator. To remove excess sodium bicarbonate, the product, sulfonated silicone  $\text{PSSO}_3\text{Na}$  was purified by repeated dialysis using 3500 Mw cut off membrane. The polymer was dried by azeotroping with benzene and in a vacuum oven at  $60^\circ\text{C}$  for 4 days.  $^1\text{H}$

NMR ( $D_2O$ ),  $\delta$  (in ppm from DHO), 4.12 (2H,  $\underline{CH_2}CH_3$ ), 2.24 (2H,  $SiCH_2CH_2\underline{CH_2}$ ), 1.42 (3H,  $CH_3$ ), 1.15 (3H,  $CH_2\underline{CH_3}$ ), 1.03 (2H,  $SiCH_2\underline{CH_2}CH_2$ ), 0.48 (2H,  $Si\underline{CH_2}CH_2CH_2$ ), -0.0 (3H,  $CH_3$ ).  $^{13}C$  NMR ( $D_2O$ ),  $\delta$  (in ppm from DSS), 171.9, 68.4, 62.8, 38.3, 19.1, 18.3, 14.7, 0.0.  $^{29}Si$  NMR ( $D_2O$ ),  $\delta$  (in ppm from DSS), -23.4.

## Results and discussion.

Methyl trimethyl silyl dimethyl ketene acetal reacts readily with the trimethylsilyl sulfonyl chloride at room temperature and affords, after hydrolysis, the sulfonate in about 90% yield. The NMR spectra suggest that only sulfonation at carbon took place.

Hydrosilation of PMHS with ETMA proceed in high yield as indicated by the absence of the Si-H stretch adsorption at  $2160\text{ cm}^{-1}$  in IR and the Si-H resonance peak at 4.01 ppm in the NMR spectra. The sulfonation of ETMA-modified polysiloxane has a lower conversion than that of model reaction, because of the steric hindrance of the polymer chain. The yield of the sulfonation can be calculated from  $^1H$  NMR and elemental analysis. When the ratio of reactants is 1, for four hours reaction, the calculated conversion from NMR data is about 76%. The presence of a single  $^{29}Si$  NMR peak at ca. -22 ppm argues against significant cleavage of the polymer under hydrolysis conditions.

## Conclusions.

Reactions of silyl ketene acetal modified silicones with trimethyl silyl sulfonyl chloride can conveniently afford water soluble silicones. The properties of these new materials and partially sulfonated copolymers is under investigation.

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